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NITRATION REACTIONS OF ETHYL CENTRALITE

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NITRATION REACTIONS OF ETHYL CENTRALITE

by

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RESUME

On décrit des expériences préliminaires où l'action de l'acide nitrique de différentes concentrations sur la centralite d'éthyle, un stabilisateur d'usage courant dans les compositions de poudres à double base, a été étudiée. Cette réaction chimique provoque la formation de plusieurs dérivés qui sont séparés, identifiés et analysés par chromatographie en couche mince et par des méthodes instrumentales usuelles. Les connaissances analytiques acquises seront utilisées dans les études de stabilité du vieillissement accéléré des poudres à canon. (NC)

ABSTRACT

Preliminary experiments are described where ethyl centralite, a stabilizer commonly used in double base propellant compositions, was reacted with nitric acid in various concentrations. The chemical transformations resulted in many derivatives which were separated, identified and analyzed by thin layer chromatography and instrumental methods. The analytical knowledge acquired will be exploited in stability studies involving artificially aged gun propellants. (U)

TABLE OF CONTENTS

ABBREVIATIONS

EC	Ethyl Centralite
4-NEC	4-Nitroethylcentralite
2-NEC	2-Nitroethylcentralite
2,2'-DNEC	2,2'-Dinitroethylcentralite
2,4'-DNEC	2,4'-Dinitroethylcentralite
2,4-DNEC	2,4-Dinitroethylcentralite
4,4'-DNEC	4,4'-Dinitroethylcentralite
2,4,4'-TNEC	2,4,4'-Trinitroethylcentralite
2,2',4,4'-TNEC	2,2',4,4'-Tetranitroethylcentralite
NEA	N-ethylaniline
2-NNEA	2-Nitro-N-ethylaniline
3-NNEA	2-Nitro-N-ethylaniline
4-NNEA	4-Nitro-N-ethylaniline
2,4-DNNEA	2,4-Dinitro-N-ethylaniline
2,4-6-TNNEA	2,4,6-Trinitro-N-ethylaniline
NNNEA	N-Nitroso-N-ethylaniline
3-NNNNEA	3-Nitro-N-Nitroso-N-ethylaniline
4-NNNNEA	4-Nitro-N-Nitroso-N-ethylaniline
2-NA	2-Nitroaniline
3-NA	3-Nitroaniline
4-NA	4-Nitroaniline
2,4-DNA	2,4-Dinitroaniline
2,4,6-TNA	2,4,6-Trinitroaniline
4-NP	4-Nitrophenol
4,4-DNC	4,4-Dinitrocarbanilide
1,3,5-TNB	1,3,5-Trinitrobenzene
Rg	$\frac{\text{Distance of sample spot from start point}}{\text{Distance of reference material spot (EC) from start point}}$
ε	Molar extinction coefficient
λ	Wavelength in nanometer (nm)

1.0 INTRODUCTION

Ethyl centralite (EC), a common designation for N,N'-diethyl-N,N'-diphenylurea, is a stabilizer frequently used in double-base gun propellants. Its function is to react irreversibly with nitrogen oxides formed during the slow decomposition of the inherently unstable nitric esters, nitrocellulose and nitroglycerine, which are the two major components of propellants. In so doing, these acidic products, which could cause auto-catalytic decomposition, are neutralized and the life of the propellant is greatly extended.

The reactions which EC undergoes during the stabilization processes are quite complicated and involve nitration, nitrosation and hydrolysis (1,2). The net result is a steady decrease of EC content and an accumulation of derivatives. The rate at which these reactions progress is primarily dependent on the environmental conditions to which the propellant is subjected during its service.

Since gun propellants have a finite life after which they are unfit for service applications or unsafe to store it is important that accurate methods be available whereby the safe life of depot holdings can be verified. Periodic inspections of this type reduce the hazards to personnel and property as well as the expense of prematurely replacing propellant stocks.

One generally accepted method for checking the chemical stability of a gun propellant is to determine the amount of residual stabilizer remaining at any particular time (3). This value becomes more and more empirical as the propellant ages because of the difficulty of separating the derivatives from the unreacted stabilizer before analysis. The values obtained, however, correlate well with the age and stability of the propellant.

A more elegant and informative method would be to separate EC and its derivatives from a propellant extract by thin layer chromatography (4). In this way the unreacted stabilizer could be analyzed in a pure form and the nitrated derivatives, many of which are highly colored, could be examined visually. The latter examination would give additional information on propellant stability since the nitro derivatives are formed in a sequential manner during ageing, that is, mono derivatives appear before dintro, etc. The appearance of higher nitrated decomposition products would indicate instability. Periodic examination of propellants in storage using this technique would provide a stability history on each propellant. The chromatographic plates could be photographed so that a continuous visual record would be available.

To test the feasibility of applying these stability tests to propellants a study, supported by Defence Research Board funding (Grant No. 9530-60), was started about four years ago at the University of Moncton, Moncton, New Brunswick. This work was subsequently supported by a contract funded under Project No. 10-28-48 "Explosives Research and Engineering". The present report summarizes the early results of this study conducted by the university in collaboration with DREV scientists.

The first part of the study dealt with the reactions of EC with nitric acid under various conditions. This preliminary work was done so that information on the stability of EC to nitric acid attack could be obtained. In addition, practice in the separation and identification of the various nitrated derivatives of EC would be useful in the subsequent examination of extracts from propellants. This paper describes the synthesis of some nitrated derivatives of EC, the techniques used for chromatographic separation, identification and analysis of the reaction products,and postulates the route by which some of them were formed.

2.0 EXPERIMENTAL

2.1 Materials and Apparatus

2.1.1 Chemicals

The following chemicals were purchased through Eastman Organic Chemicals, Rochester 3, New York: ethyl centralite (EC), N-ethylaniline (N-EA), 3-nitro-N-ethylaniline (3-NNEA), 4-nitro-N-ethylaniline (4-NNEA), 2,4-dinitro-N-ethylaniline (2,4-DNNEA), 2,4,6-trinitro-N-ethylaniline (2,4,6-TNNEA), 3-nitro-N-nitroso-N-ethylaniline (3-NNNNEA), 2-nitroaniline (2-NA), 3-nitroaniline (3-NA), 4-nitroaniline (4-NA), 2,4-dinitroaniline (2,4-DNA), 2,4,6-trinitroaniline (2,4,6-TNA), 4-nitrophenol (4-NP), 4,4-dinitrocarbanilide (4,4-DNC), 1,3,5-trinitrobenzene (1,3,5-TNB).

Derivatives synthesized at the University of Moncton included 2-nitro-N-ethylaniline (2-NNEA), N-nitroso-N-ethylaniline (N-NNEA), 4-nitro-N-nitroso-N-ethylaniline (4-NNNNEA), 4-nitroethylcentralite (4-NEC), 4,4'-dinitroethylcentralite(4,4'-DNEC) and 2,2',4,4'-tetranitroethylcentralite (2,2',4,4'-TNEC). The methods of synthesis are described in Sec. 2.2.

Other ethylcentralite derivatives such as 2-nitroethylcentralite (2-NEC), 2,2'-dinitroethylcentralite (2,2'-DNEC), 2,4'-dinitroethylcentralite (2,4'-DNEC), 2,4-dinitroethylcentralite (2,4-DNEC) and

2,4,4'-trinitroethylcentralite (2,4,4'-TNEC) were not available commercially and proved difficult to synthesize in sufficient quantity for definite characterization. Detailed examination by thin layer chromatography of residues from nitration experiments, however, provided sufficient material for partial spectral examination and recording of Rg values. Comparison of these results with values obtained from the chemical literature (Tables I and II) allowed tentative assignments to be made.

2.1.2 Absorbents

To obtain sufficiently pure samples for melting point determinations the absorbent used with column chromatography was alumina or a mixture of silicic acid-celite 535. In the thin layer chromatographic separations Silica Gel G (Brinkman Instruments) was used.

2.1.3 Equipment

The thin layer chromatographic equipment consisted of a Desaga Spreader Model S-11, glass plates, template and glass tanks purchased from Brinkman Instruments. Ultraviolet sources consisted of two lamps (366 and 253 nm) purchased from Ultraviolet Products Inc., San Gabriel, California.

Visible and ultraviolet absorption spectra were determined on a Beckmann DB spectrophotometer using 95% ethanol as a solvent.

2.2 Procedures

2.2.1 Synthesis and characterization of ethyl centralite (EC) derivatives and possible degradation products

The synthesis of 4-nitroethylcentralite (4-NEC) was accomplished by dissolving EC (5 g) in glacial acetic acid (15 ml) and concentrated H_2SO_4 (5 ml) and nitrating with a mixture of 0.5 N HNO_3 (30 ml) and concentrated H_2SO_4 (5 ml) which was added in drops over a period of 30 min. The reaction was allowed to proceed for one hour and the solution was poured into crushed ice. After neutralizing with NaOH the reaction products were extracted with ethyl ether and the solvent evaporated. A viscous oil was obtained. The oil was dissolved in 2:1 benzene/petroleum ether and chromatographed on a 2:1 silicic acid/celite column using 1:4 ether/petroleum ether as developer. After development with 50 ml of solvent a yellow band was observed which broadened as it reached the lower part of the column. This was followed by a second reddish-brown band which moved slowly. The yellow oil obtained was rechromatographed using the procedure described above and the recovered product was crystallized from 2:1 ethanol/petroleum ether to give 4-NEC: λmax., 333.5 nm, ε, 7,990. Lit. λ max., 334-335 nm, ε, 8340 (5).

TABLE I

R_g Values for Ethyl Centralite, its Nitro Derivatives and Possible Degradation Products

Compound	Values (observed) S_1	Values (observed) S_2	Values (Literature)[a] S_1	Values (Literature)[a] S_2
EC[b]	1.00	1.00	1.00	1.00
4-NEC	2.80	0.69	2.40	0.64
2-NEC	1.80	0.80	1.60	0.74
2,2'-DNEC	2.50	0.46	2.20	0.30
2,4'-DNEC	3.60	0.52	3.55	0.44
4,4'-DNEC	3.50	0.38	3.55	0.25
2,4-DNEC	2.75	0.40	2.25	0.30
2,4,4'-TNEC	5.00	0.35	4.50	0.24
2,2',4,4'-TNEC	4.40	0.55	4.50	0.50
2-NNEA	8.80	1.30	10.50	1.45
4-NNEA	7.50	0.75	7.60	0.82
2,4-DNNEA	8.00	0.69	9.50	0.68
2,4,6-TNNEA	7.90	0.99	10.25	1.35
4-NA	5.80	0.46	5.90	0.30
3-NA	5.30	0.70	--	--
2,4-DNA	5.75	0.38	5.70	0.25
1,3,5-TNB	8.00	1.20	9.00	1.41
4-NP	2.10	0.40	1.90	0.24

(a) Values estimated from Ref. 4

(b) EC used as reference.

(c) S_1 Development with ethylene dichloride.

(d) S_2 Development with petroleum ether/ethyl acetate (75:25).

Rechromatographing the second reddish-brown band by the method described above but using more polar solvent did not result in separation although examination by thin layer chromatography (Sec. 2.2.3) showed the presence of two compounds, one of which was determined to be 4,4'-DNEC by comparing its spectral and chromatographic properties with an authentic sample, the synthesis of which is subsequently described. The second compound was tentatively identified as 2,4'-DNEC on the basis of thin layer chromatographic behavior (4). This derivative proved to be impossible to isolate by column chromatography and therefore an insufficient quantity was obtained for complete characterization during this study.

To obtain the 4,4'-dinitro derivative EC (5 g) was dissolved in a mixture of acetic acid (45 ml) and concentrated H_2SO_4 (5 ml). After cooling to 10°C a mixture of 15N HNO_3 and concentrated H_2SO_4 (5 ml) was added drop by drop over a period of 30 min. The reaction was continued for a further 30 min and the dark mixture was poured onto crushed ice. The excess of acid was neutralized with NaOH and the solution extracted with ether. Upon evaporation a dark residue was obtained, which was taken up in 2:1 benzene/petroleum ether and chromatographed on a 2:1 silicic acid/celite column using 1:2 ethyl ether/petroleum ether as developer. A deep yellow band appeared, which moved very slowly with broadening, followed by a second brown band which separated slightly from the top of the column. The lower band was eluted and the product was shown by thin layer chromatography to be a mixture containing 4-NEC. The material was dissolved in benzene and chromatographed on a column containing alumina using 6:1 benzene/petroleum ether as a developer. Two colored bands were observed. The lower was shown to be 4-NEC and the upper band contained 4,4'-DNEC. Three recrystallizations of the latter material gave bright yellow platelets: m.p. 147°C., Lit. m.p. 147°C., λmax., 323.5 nm, ε, 15,200. Lit. λmax., 323-324 nm, ε, 15,200 (1).

The upper band was eluted with ether, taken to dryness, dissolved in 2:1 benzene/petroleum ether and rechromatographed on an alumina column using 6:1 benzene/petroleum ether as developing solvent. Two broad zones separated. The lower upon elution and examination by thin layer chromatography contained two compounds which from their chromatographic behaviour were tentatively identified as 2,4' and 2,2'-DNEC.

The upper band was examined in a similiar manner and found to contain two compounds. One was identified as 2,2',4,4'-TNEC by comparing its properties with those of an authentic compound. The other was tentatively identified as 2,4,4'-TNEC on the basis of partial spectral evidence and thin layer chromatographic behaviour.

TABLE II

Spectral Data for Ethyl Centralite, its Nitro Derivatives and Possible Degradation Products

Compounds	Values (observed)		Values (Literature)[a]	
	λ max, nm	ε[b]	λ max, nm	ε
EC	247	8,730	247	8,730
4-NEC	246	--	245-247	12,400
2-NEC	333.5	7,990	334-336	8,240
2,4'-DNEC	323.5	--	--	--
4,4'-DNEC	323.5	15,200	323-324	15,200
2,4,4'-TNEC	308.5	--	309-310	14,400
2,2',4,4'-TNEC	293	11,800	--	--
NEA	247	11,000	247	11,100
2-NNEA	425.5	6,200	425	5,200
3-NNEA	246.5	17,800	244	19,100
4-NNEA	385.5	19,000	385-386	19,300
2,4-DNNEA	347	16,700	347-348	16,600
2,4,6-TNNEA	336	15,000	336	14,900
N-NNEA	272	6,600	271	6,800
4-NNNEA	313	18,800	312-314	14,900
2-NA	404	--	403-406	5,400
3-NA	375	1,500	375	1,500
4-NA	371.5	16,100	373-375	16,400
2,4-DNA	336	14,900	336	14,800
1,3-DNB	237.5	--	--	--
1,3,5-TNB	227	--	--	--
4-NP	312	11,800	312	11,900

(a) Refs. 1 and 5

(b) ε, molecular extinction coefficient

The synthesis of 2,2',4,4'-TNEC was achieved by dissolving 4,4'-DNEC in concentrated H_2SO_4 (5 ml) and adding drop by drop over a period of 30 min a mixture containing concentrated H_2SO_4 (4 ml) and 15N HNO_3 (5 ml). The reddish solution was heated to 50°C on a hot plate, allowed to cool to room temperature and poured onto ice. The solid which separated was washed several times with water and recrystallized from ethyl alcohol to give bright yellow needles of pure 2,2',4,4'-TNEC: m.p. 177-178°C, Anal. Calc. for $C_{17}H_{16}N_6O_9$:C,45.54%;H,3.57%;N, 18.75%. Found: C,45.50%; H, 3.60%; N, 18.73%.

2-Nitro-N-ethylaniline (2-NNEA) was obtained by refluxing ρ-toluene sulphonyl-o-nitroaniline with diethyl sulfate in 6N NaOH and after cooling the reaction product was extracted in ether. The solvent was evaporated and the residue dissolved in benzene and chromatographed on an alumina column using benzene as developer. The reddish band obtained was eluted and the desired compound was obtained as an oil: λmax. 425.5 nm, ε, 6,200, Lit. λ max, 425 nm, ε, 6,200 (5).

N-nitroso-N-ethylaniline (N-NNEA) was obtained by nitrosation of N-ethylaniline (NEA). The reaction was done in the cold and consisted of adding an aqueous solution of $NaNO_2$ to the starting material which was dissolved in concentrated HCl. The product was extracted with ether, the solvent evaporated and the residual liquid distilled to give a yellow oil: b.p. 131°C/18 torr, λmax., 272 nm, ε, 6,600, Lit. b.p. 131°C/20 torr, (6), λmax., 271 nm, ε, 6,800 (5).

The corresponding nitro derivative, 4-nitro-N-nitroso-N-ethylaniline (4-NNNNEA) was synthesized from 4-nitro-N-ethylaniline (4-NNEA) in a similar manner: m.p. 117-118°C., λmax., 313 nm, ε, 18,800, Lit. m.p. 119-120°C., (1), λmax., 314 nm, ε, 17,900 (5).

2.2.2 Detailed nitration and hydrolysis studies of ethyl centralite

The general procedure involved dissolving EC (1 g) in glacial acetic acid (45 ml) and cooling the solution to 5°C in a flask equipped with a mechanical stirrer and a dropping funnel. Concentrated H_2SO_4 (15 ml) was added slowly followed by a nitrating mixture. The nitrating mixture consisted of H_2SO_4 (10 ml) and nitric acid (30 ml), the latter varying in strength from 0.1 N to 15.0 N. Reaction time was 40 min following the addition of all reagents. The reaction was quenched by pouring the mixture onto crushed ice. The excess acid was neutralized with Na_2CO_3 and the resulting products extracted with ethyl ether. The extract was dried over Mg SO_4 and the solvent evaporated. The residue was redissolved in acetone and examined by thin layer chromatography.

2.2.3 Thin-layer chromatography techniques and quantitative analysis

Silica Gel G absorbent was agitated in water until a homogeneous slurry was obtained. This was applied to glass plates to obtain an absorbent layer 0.3 mm thick. The plates were dried in air, activated at 120°C in an oven and stored in a dry container until used.

The residues from the nitration of EC were dissolved in acetone and a microliter sample was quantitatively applied to the chromatographic plate and the solvent allowed to evaporate. The plates were placed in the developing tanks and treated by ascending development using ethylene dichloride as developer. To obtain sharper separations the plate was taken out of the tank, dried in air, and rechromatographed in a 90° direction to the first development using 75:25 petroleum/ethyl acetate solvent. After drying the various nitrated products were located by viewing the plate under short- and long-wavelength ultraviolet light. Based on the position of the spots tentative identifications were made by comparison of RG values with those obtained using authentic samples (Table I). The spots were removed using a small spatula and the absorbent was extracted with 95% ethanol. The extract was examined by ultraviolet spectroscopy to positively identify and analyze the product where authentic reference data was available (TableII). In some cases where complete reference data was not available the results must be considered to be less reliable. Spot sizes were used in some cases to obtain semi-quantitative data employing the Desaga template.

Some of the results obtained on separating nitrated derivatives of EC after treatment with nitrating solutions of increasing strength are shown in Figs 1 and 2.

Quantitative estimations of the various nitrated compounds derived from EC are shown in Table III.

Proposed routes by which the various derivatives could form are shown in Figs 3,4 and 5.

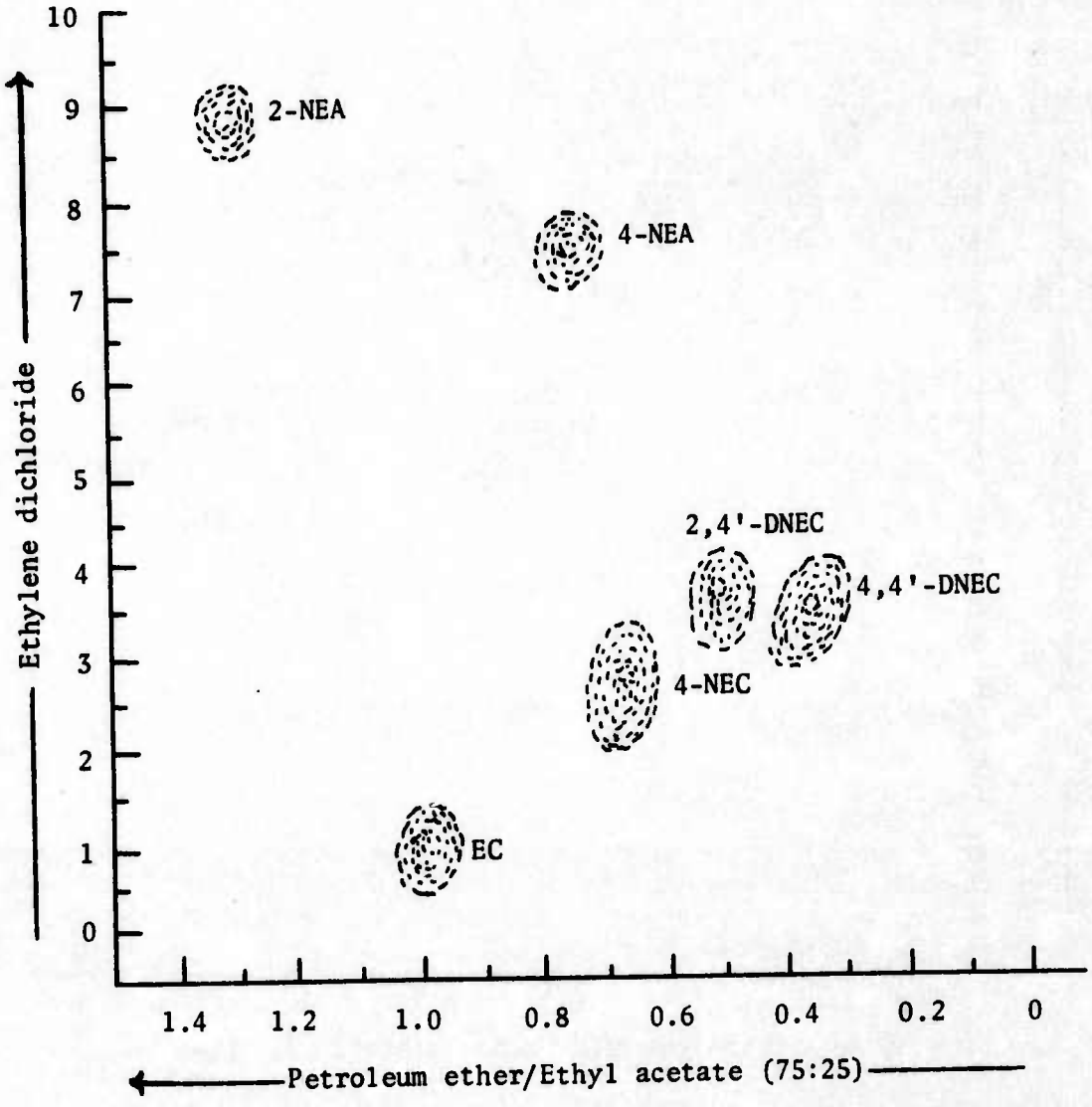

FIGURE 1 - Two dimensional thin-layer chromatogram of a mixture obtained from nitration of ethyl centralite using 0.5 N HNO_3

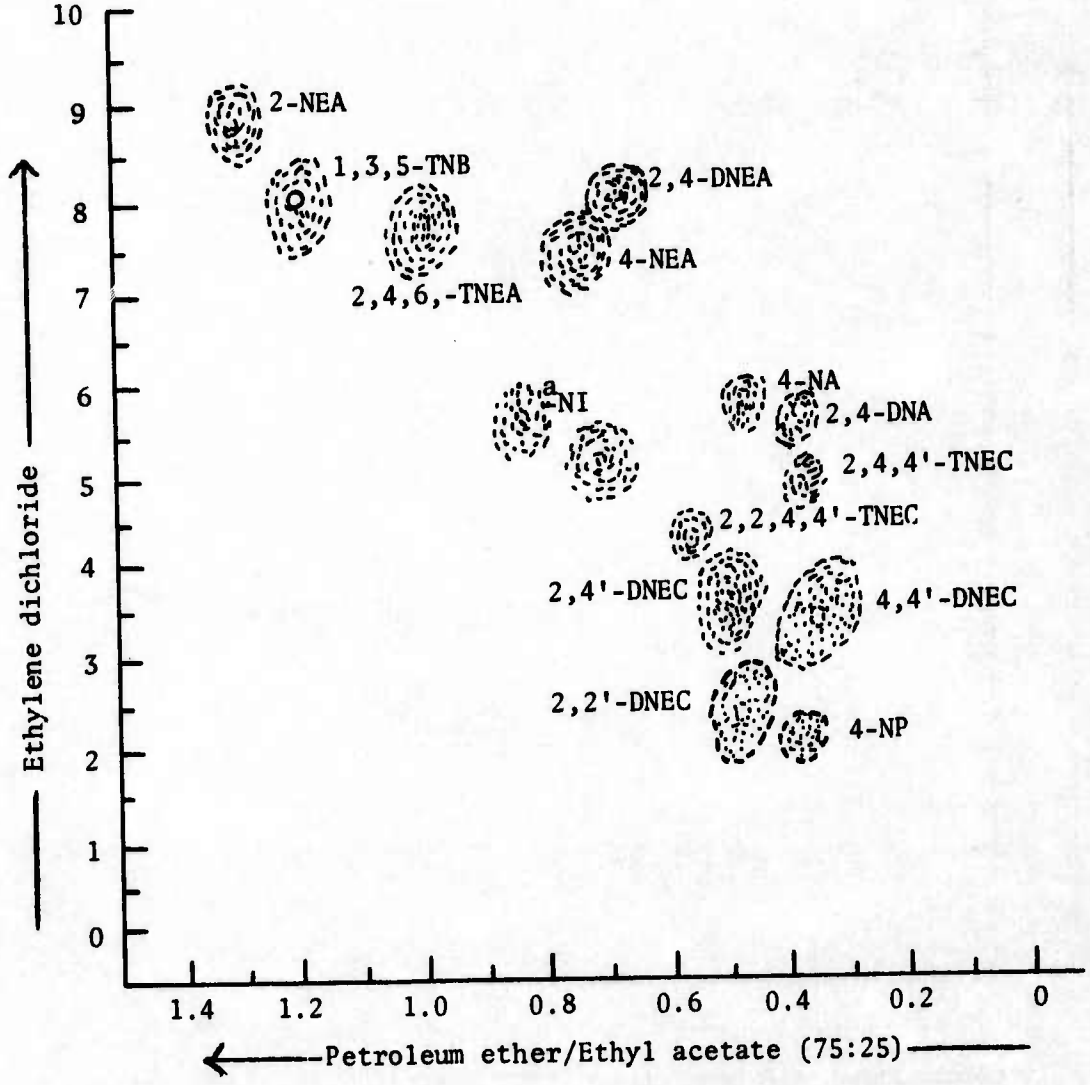

FIGURE 2 - Two dimensional thin-layer chromatogram of a mixture obtained from nitration of ethyl centralite using 15 N HNO_3

NI - not identified

TABLE III

Recovery of Products from the Nitrations of Ethyl Centralite

Nitrating Agent	Recovery (%)[a]																
HNO_3	EC	4-NEC	2NEC	2,2'-DNEC	2,4'-DNEC	4,4'-DNEC	2,4,4'-TNEC	2,2',4,4'-TNEC	2NNEA	4-NNEA	2,4-DNNEA	2,4,6-TNEA	4-NA	3-NA	2,4-DNA	1,3,5-TNB	4-NP
0.1N	98½0	T[b]	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
0.5N	16.1	36.4	--	--	12.6	12.6	--	--	T	0.2	--	--	--	--	--	--	--
1.0N	--	T	--	--	46.8	38.4	--	--	T	0.7	T	T	--	--	--	--	--
2.0N	--	--	--	T	47.0	37.4	--	--	0.4	0.8	T	T	T	--	--	--	--
4.0N	--	--	--	2.0	33.4	48.0	T	--	0.5	1.1	T	0.3	T	--	--	--	--
6.0N	--	--	--	4.3	23.9	51.5	T	--	0.6	1.0	0.2	0.4	T	--	--	--	--
8.0N	--	--	--	4.5	23.0	49.4	T	--	1.1	0.8	0.8	0.5	T	--	--	--	--
10.0N	--	--	--	4.9	18.2	56.0	0.4	T	1.0	0.7	2.1	0.7	T	T	T	--	--
15M	--	--	T	6.2	18.4	54.8	2.6	7.5	1.1	0.3	0.6	1.2	0.2	T	T	T	T

(a) With the exception of the first nitration, tars were also formed.

(b) Trace.

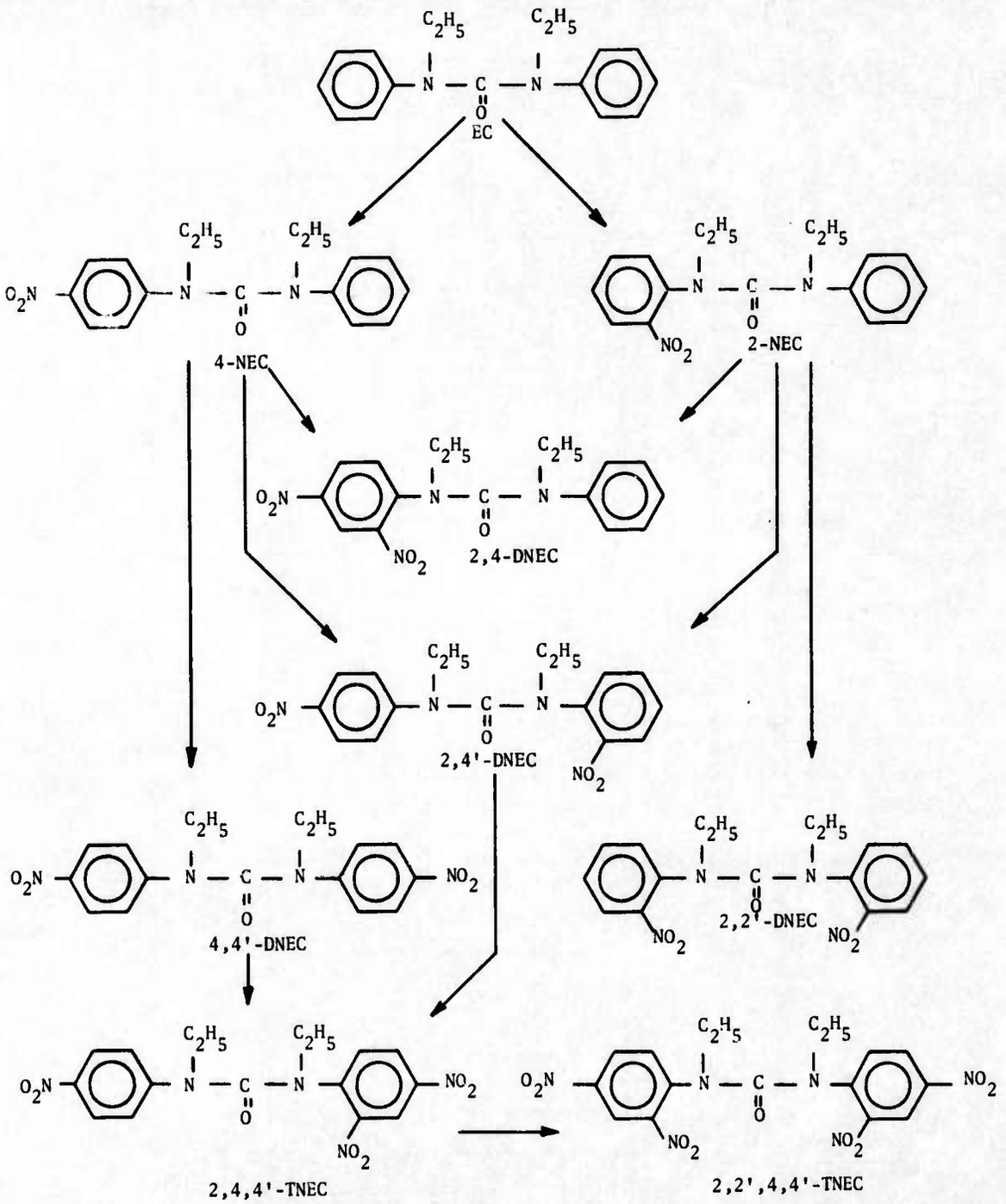

FIGURE 3 - Probable routes for the formation of nitroethyl centralites

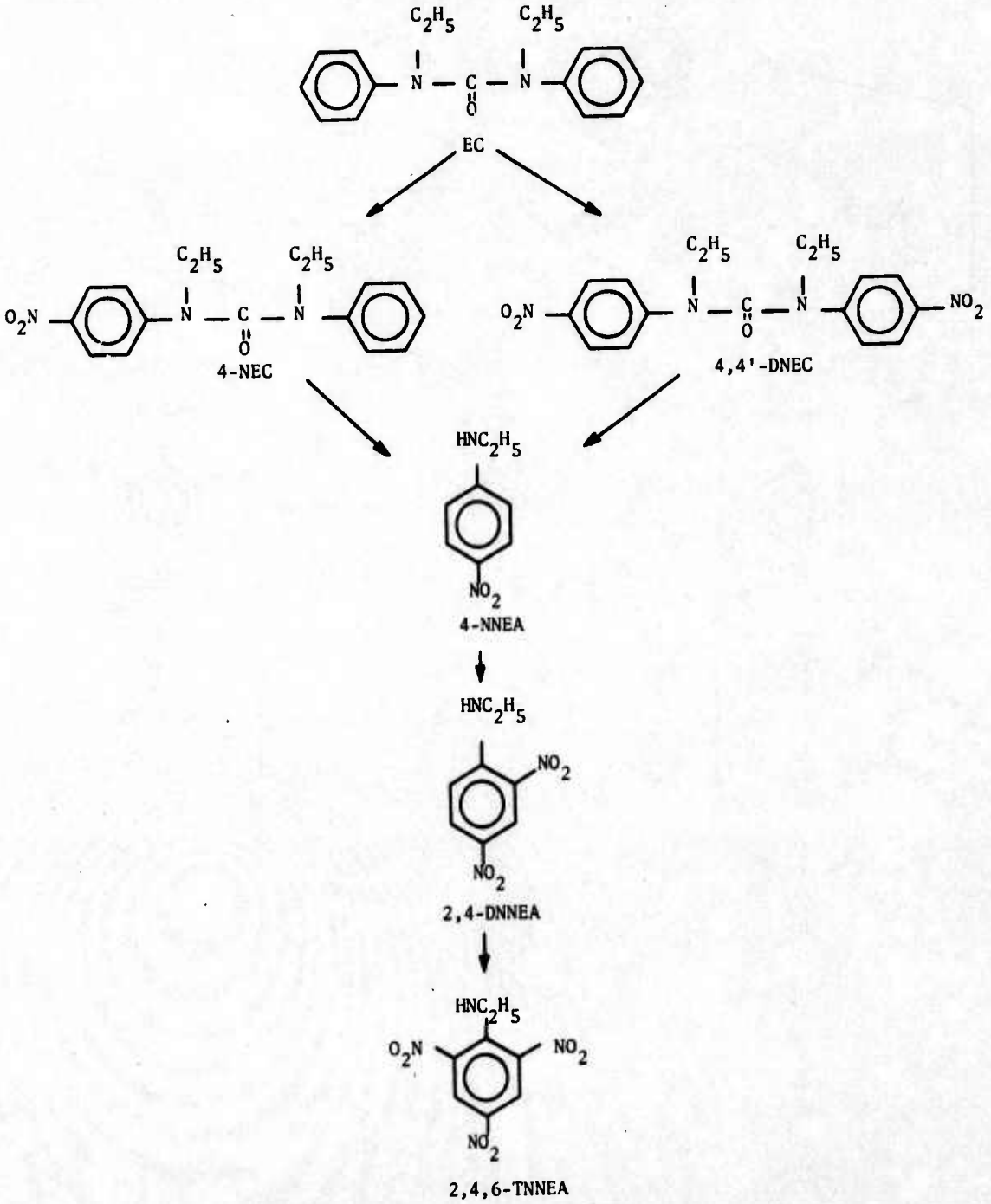

FIGURE 4 - Probable routes for the formation of 4-Nitro, 2,4-Dinitro and 2,4,6-Trinitro-N-ethylaniline

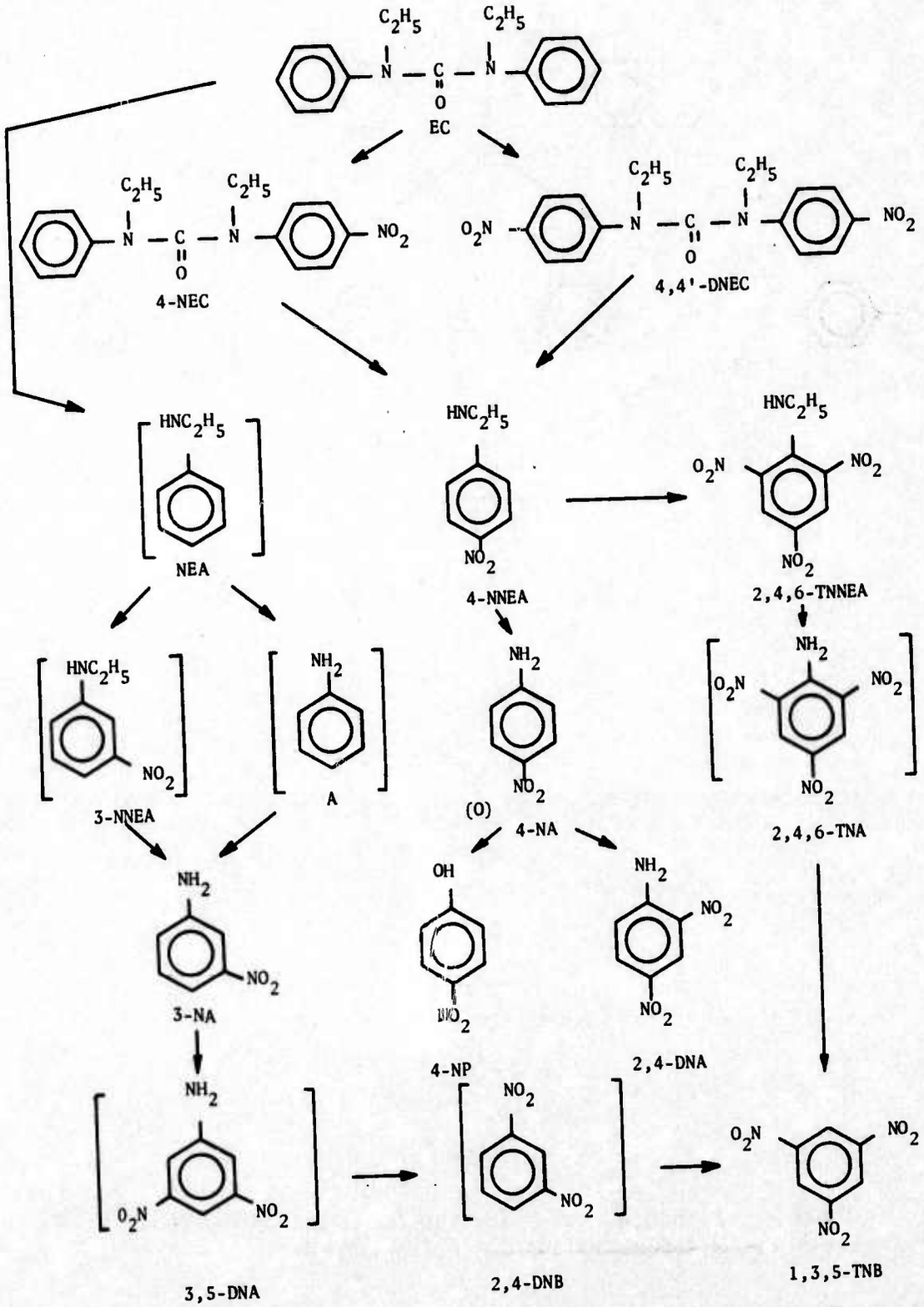

FIGURE 5 - Probable routes for the formation of minor degradation products

3.0 RESULTS AND DISCUSSION

The increased complexity of the products obtained by nitrating EC with 0.5 N and 15 N HNO_3 may be appreciated by examination of Figs 1 and 2. Treatment with the dilute nitrating solution produced five derivatives while reaction with the more concentrated reagent produced fifteen compounds. Examination of Table III gives a detailed account of the order in which these derivatives arose during treatment of the parent material with nitrating agents of increasing concentrations.

It may be seen from Table III that treatment with 0.1 N HNO_3 had little effect; unreacted EC and a trace of 4-NEC was recovered. Increasing the concentration fivefold gave some unreacted EC, 4-NEC, 4,4'-DNEC and 2,4'-DNEC along with trace amounts of two hydrolysis products, namely, 2- and 4-NNEA. It is apparent that the formation of 4-NEC is favoured and that this compound is the precursor of the two dinitro derivatives. The two degradation or hydrolysis products could be formed from cleavage of 4-NEC, 4,4'-DNEC or 2,4'-DNEC. Hydrolysis of the substituted derivatives because of the electron attracting nature of the nitro group is favoured rather than prior hydrolysis of EC followed by nitration.

EC was completely consumed by treatment with 1 N HNO_3 under the standard conditions. The two major products were 4,4'-DNEC and 2,4'-DNEC. The presence of 4-NEC was reduced to trace amounts and in addition to the products of hydrolysis observed in the previous experiment, two higher nitrated derivatives, namely 2,4-DNNEA and 2,4,6-TNNEA, were identified. It is apparent from Table III that the two dinitro derivatives of the parent material were formed at the expense of 4-NEC. The appearance of 2,4-DNNEA can be attributed to cleavage of 4,4'-DNEC followed by nitration of 4-NNEA or hydrolysis of 2,4'-DNEC and subsequent nitration of 2- and/or 4-NNEA. The 2,4,6-TNNEA can only arise by way of the 2,4-dinitro analogue.

Nitration with 2 N HNO_3 completely transformed 4-NEC. The yields of 2,4' and 4,4'-DNEC remained about constant and a trace of 2,2'-DNEC was tentatively identified. The yield of 4-NNEA, 2,4-DNNEA and 2,4,6-TNNEA remained essentially unchanged but that of 2-NNEA increased fourfold. A trace of 4-NA was also detected. The absence of 4-NEC is probably due to its conversion to dinitro derivatives, nitration having occurred preferentially at the ortho and para positions in the unsubstituted benzene ring. The formation of 2,2'-DNEC could only be explained on the basis of direct nitration of EC, although in this case one might have expected to observe 2-NEC as one of the reaction products. However, subsequent complete conversion of the latter substance to 2,4'-DNEC would explain its absence. The 4-NA was likely formed by de-ethylation of 4-NNEA.

Nitration with 4 N HNO_3 gave the same products along with a trace of 2,4,4'-TNEC. The yield of 4,4'-DNEC increased while that of the 2,4'-isomer decreased. In addition the percentage of 2,2'-DNEC increased sharply while the minor ingredients 2-NNEA, 4-NNEA and 2,4,6-TNNEA appeared in higher quantities. The 2,4,4'-TNEC likely arose from the 2,4'-analogue since the latter decreased in yield during this experiment.

Continuing the nitration of EC with 6 and 8 N NHO_3 produced the same derivatives in different yields except that 2,4-DNA was detected in the latter experiment. This new derivative was likely formed by nitration of 4-NA which was also present in the mixture.

The products obtained with 10 N HNO_3 included those identified in the previous experiment with the addition of traces of 2,2',4,4'-TNEC and 3-NA. The most probable route to the tetranitro derivative appears to be nitration of the 2,4,4'-trinitro compound which showed a decrease in yield during this experiment. The presence of 3-NA was unexpected because the precursors which require nitration in the 3-position are not easily formed. It is conceivable that protonation of the parent compound occurred, directing the nitro group to the 3-position. The parent compounds could be EC, NEA formed by hydrolysis or aniline formed from the latter by de-ethylation.

Treatment of ethyl centralite with 15 N HNO_3 produced sixteen products, some fifteen of which were identified. The two dimensional thin layer chromatogram of the mixture is shown in Fig 2. Additional nitrations at the expense of lower substituted derivatives were indicated by marked increase in 2,4,4'-TNEC and 2,2',4,4'-TNEC. In addition to the minor degradation products reported above traces of 2-NEC, 1,3,5-TNA, 4-NP and an unidentified compound S were detected. The 2-NEC which was detected for the first time in these experiments can only arise from EC. The presence of 4-NP can be attributed to the oxidation of the corresponding 4-nitro-aniline. The 1,3,5-TNB on the other hand could be formed by de-ethylation and deamination of 2,4,6-TNNEA. It could also be produced from 3-NA by nitration to the 3,5-dinitro derivative, deamination and further nitration. It should however be pointed out that neither 2,4,6-TNA nor 1,3-DNB were detected in this or previous nitration experiments.

4.0 CONCLUSIONS

Some interesting general conclusions can be drawn from the experimental data accumulated during this study. Thus, direct nitration of ethyl centralite to the 4-nitro derivative and subsequent reaction to form 4,4'-dinitro and 2,4'-dinitro compounds is the major reaction pathway. Relatively little further nitration to tri and tetranitro derivatives occurred and, although several degradation products were observed, these transformations were not of major significance. It is also clear that both the degree of nitration and degradation increased with the concentration of HNO_3 employed.

Although these experiments can not be directly related to ageing processes which occur in gun propellants it is evident that most of the centralite derivatives separated and analyzed in the course of our experiments have been isolated or postulated by other workers in the propellant stability field. The knowledge gained during our study, in particular the separation and analytical procedures, will prove to be of great value when examining and assessing the stability or safelife of gun propellants which have undergone natural or accelerated ageing.

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